Uptake of Aromatic Solvents by Polyethylene Films

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ABSTRACT: The sorption properties of the solvents benzene, toluene, and xylene in polyethylene films at 40, 60, and 80°C were investigated. The diffusion coefficient increased with an increase in the sorption temperature for the solvents and was highest for xylene and least for benzene. The inability of xylene to show a definite order of the diffusion coefficients at the investigated temperatures was attributed to the presence of two methyl side groups in the molecule. The solubilities of the solvents in polyethylene increased with an increase in the sorption temperature, and the following order of the solubilities could be observed: xylene > toluene > benzene. The permeabilities of the solvents in polyethylene depended on the sorption temperature, and the following order of the permeabilities was observed: xylene > toluene > benzene. The calculated activation energies of sorption in polyethyl- ene films were all positive; benzene had the highest energy of sorption, and xylene had the lowest. The calculated enthalpies of sorption (ΔH_S) were also positive for the three solvents and were in the following order: xylene > toluene > benzene. The calculated entropies of sorption (ΔS) were negative for the solvents and showed trends similar to the variation of ΔH_S among the solvents. The change in the Gibbs free energies of sorption (ΔG_S), evaluated with the expression $\Delta G_S = \Delta H_S - T\Delta S$ (where T is the Kelvin temperature), were all positive, and this was an indication of the nonspontaneity of the solubility of polyethylene in the aromatic solvents at 313 K. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3849–3854, 2007

Key words: activation energy; diffusion; films; polyethylene (PE)

INTRODUCTION

Diffusion is a molecular process by which a concentration gradient induces a flux of penetrant molecules from regions of high concentration to regions of low concentration. Because of the importance attached to the diffusion of organic (solvent) molecules through polymeric films, numerous research works have been reported in the scientific literature for a variety of polymer–solvent systems with reference to their transport-based sorption. The knowledge gained from these diffusion studies has been used in microelectronics,[1] food processing,[2,3] controlled drug release,[4,5] polymer processing industries,[6] and separation science.[7,8] Other areas include the concentration of sea water and the treatment of effluent water.[9]

Polymers absorb solvents to various degrees. The absorption of a solvent causes a polymer to increase in volume; as a result, the physical properties deteriorate. The swelling of plastics is a diffusion process. Factors that affect diffusion in polymers have been identified, and they include the following: the degree of solvent–polymer interactions and solvent properties such as the solvent size and shape, hydrogen bonding, polarity, and solubility parameter.

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Fick's first and second laws were developed to describe the diffusion process in polymers. Fickian or case I transport is obtained when the local rate of change in the concentration of a diffusing species is controlled by the rate of diffusion of the penetrant. For most purposes, diffusion in rubbery polymers typically follows Fickian law.[10] Polymer segments in their glassy states are relatively immobile and do not respond rapidly to changes in their conditions. These glassy polymers often exhibit anomalous or non-Fickian transport. When the anomalies are due to an extremely slow diffusion rate versus the rate of polymer relaxation, the non-Fickian behavior is called case II transport.

Polyethylene is the most popular plastic in the world. It is probably the plastic most often encountered in daily life. It is used to make grocery bags, shampoo bottles, children's toys, and even bullet-proof vests. Because of polyethylene's wide range of applications, some of which bring it into contact with various solvents, numerous sorption studies have been carried out with different solvents for solvent uptake in polyethylene films. Thus, Huang and coworkers[11,12] reported that the molecular size and shape of solvent molecules affect permeation through polyethylene films, whereas Laine and Osburn[13] correlated the permeation of organic vapors through polyethylene films with the molar volume of the liquid and the membrane–liquid interaction.

TABLE I
Properties of the Solvents

Solvent	Density (g/cm^3)	Molecular mass volume (g/mol)	Dipole moment (D)	Solubility parameter (MPa$^{1/2}$)
Benzene	0.8790	78.12	0	18.7
Toluene	0.8661	92.14	0.36	18.3
Xylene	0.8650	106.17	0.70	18.2

The permeation of organic vapors through a polymer membrane (low-density polyethylene) at 25–40°C has been reported.[14] From experimental data, appropriate permeation and diffusion coefficients have been calculated.

Machkova et al.[15] studied the sorption of organic vapors (methanol, ethanol, chloroform, and acetone) in flat and high-pressure low-density polyethylenes at 25°C. The sorption of chloroform in both membranes was reported to be much higher than the sorption of the other vapors. The permeability coefficients of saturated and nonsaturated vapors (hexane, heptane, cyclohexane, benzene, and toluene) through low-density polyethylene were studied by Friess et al.[16] Izak et al.[17] used various models to describe the transport of binary liquid mixtures (pentan-1-ol and hexan-1-ol with toluene) through low-density polyethylene membranes at 25°C; moreover, the influence of the number of carbon atoms of aliphatic alcohols (ethanol, propan-1-ol, and butan-1-ol) on transport parameters in polyethylene has been reported.[18]

In similar studies, De Fillippi[19] and Choo[20] reported that the solvent annealing of polyethylene increases film permeability to xylenes and chlorohydrocarbons, whereas Krewinghauss[21] showed that uniaxially cold-drawn polyethylene films exhibited a significant increase in permselectivity to benzene versus cyclohexane.

In this work, the sorption characteristics of the homology of the aromatic solvents benzene, toluene, and xylene in polyethylene films at 40, 60, and 80°C are reported. This study provides an example of how gradual changes in the solvent properties (molecular weight, polarity, molar volume, etc.) and solvent structures affect the diffusion of organic solvents into polyethylene films. The effects of the temperature on the solvent diffusion parameters are also reported.

EXPERIMENTAL

Materials

The polyethylene films used in this work were obtained from the Plastic Technology Development Centre of Eleme Petrochemical Co., Ltd. (Rivers State, Nigeria). The polyethylene film had a melt index of 0.5 dg/min and a mean molecular weight of 200,000–400,000. The approximate thickness was 0.168 mm. The analytical-grade solvents were benzene and toluene (both from BDH Chemicals, Ltd., Poole, England) and xylene (Wilkinson Vickers, Ltd., West Yorks, England).

Procedure for the sorption experiment

Approximately 0.10 g of the polyethylene film sample was weighed and put into a sample bottle with a cover. Twenty milliliters of benzene, toluene, or xylene was poured into the sample bottle. The thermostatic water bath was equilibrated at 40, 60, or 80°C for the sorption experiment. After equilibration at the required temperature, the sample bottle containing the film was put into the equilibrated water bath and allowed to equilibrate for the time required. At the expiration of the required time, each film was removed from the bottle with tweezers. The solvents adhering to the surface of the polyethylene films were removed by careful pressing of the films between filter paper wraps. Care was taken to ensure that the solvents absorbed by the film were not removed during the process of wiping with the filter paper. The wet film was weighed, and the difference between the dry film and the wet film was obtained. All the weighing was carried out with a Sartorius model A 200 S balance (Gottingen, Germany) with a precision of ±0.1 mg.

RESULTS AND DISCUSSION

The properties of the solvents (benzene, toluene, and xylene) used in this study are presented in Table I.

The sorption data for the polyethylene films at 40, 60, and 80°C were determined and expressed as the molar percentage uptake (Q_t) of the solvent per gram of the polymer as follows:[21,22]

$$Q_t = [(\text{Mass of the absorbed solvent}/$$
$$\text{Molecular weight of the solvent})/$$
$$\text{Mass of the polymer}] \times 100 \quad (1)$$

Q_t at any particular temperature was plotted against the square root of time ($\sqrt{t}$) and is shown in
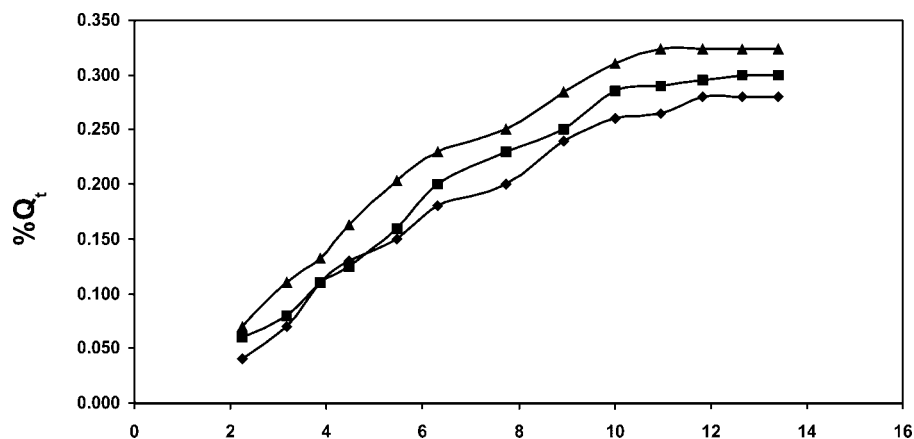
Figure 1 Q_t for benzene versus $\sqrt{t}$ at different temperatures: ($\blacklozenge$) 40, ($\blacksquare$) 60, and ($\blacktriangle$) 80°C.

Figures 1–3. These figures show initial increases in the mass of the solvent sorbed until the maximum absorption was reached, at which time the mass of the absorbed solvent remained constant (i.e., equilibrium absorption was attained). The higher initial solvent absorption rates in polymers have been explained in terms of rapid cavitation, which exposes a greater surface area, thus enhancing solvent permeation.[24] On the other hand, at equilibrium, the solvent uptake is counterbalanced by solvent extraction from the polymer.

Figures 1–3 show that the solvent uptake for any particular solvent increases with an increase in temperature. This is expected because the movement of diffusing solvent molecules is facilitated by the higher thermal energies at the increased temperature.[25] This results in a subsequent reduction in the viscosity of the solvents and a further increase in the segmental mobility of the polymers.

Analysis of the sorption data

Diffusion coefficient

The diffusion coefficient (D) of a solvent molecule in a network of a polymer can be obtained with Fick's second law of diffusion:[26]

$$D = \pi(h\theta/4Q_\infty)^2 \tag{2}$$

where h is the polymer film thickness, θ is the slope of the initial linear portion of the plot of $^\circ/Q_t$ versus $\sqrt{t}$, and Q_∞ is the equilibrium absorption.

The diffusion coefficients for the three solvents (benzene, toluene, and xylene) at the different temperatures studied are given in Table II. From Table II, for the solvents benzene and toluene, the diffusion coefficient was observed to increase with an increase in the temperature. This is in general agreement with the findings of Uzomah and Ibrahim,[26] who
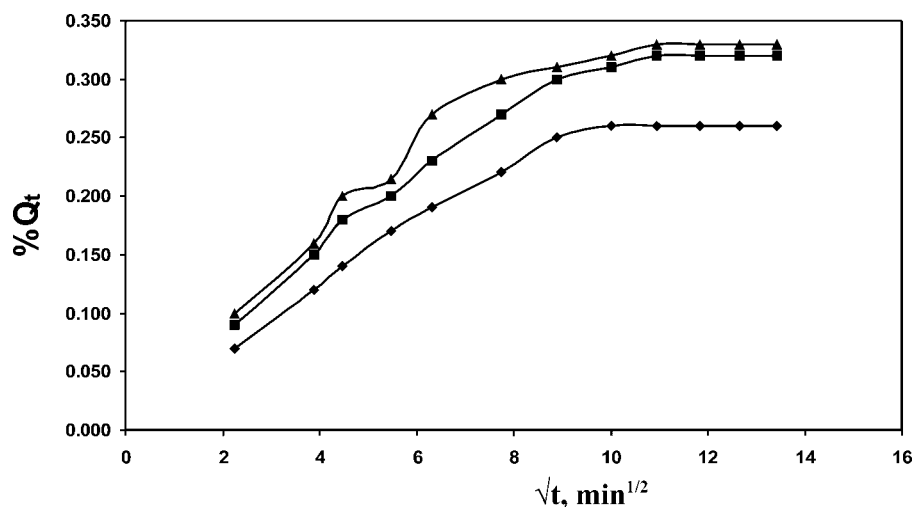
Figure 2 Q_t for toluene versus $\sqrt{t}$ at different temperatures: ($\blacklozenge$) 40, ($\blacksquare$) 60, and ($\blacktriangle$) 80°C.
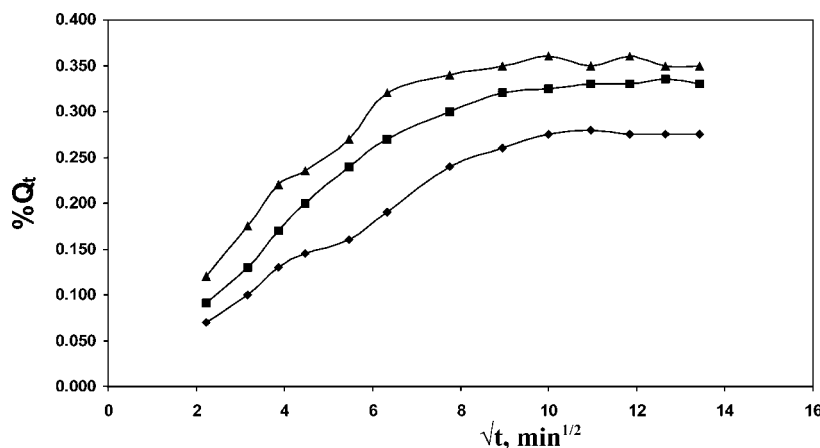
Figure 3 Q_t for xylene versus $\sqrt{t}$ at different temperatures: (◆) 40, (■) 60, and (▲) 80°C.

reported that the diffusivities increased with an increase in the temperature. The diffusion coefficient was found to decrease from 40 to 60°C for the solvent xylene and thereafter increased at 80°C. It is well known that the shape of a solvent molecule affects its transport properties.[28–30] In this study, the inability of the solvent xylene to show a definite order of the diffusion coefficients at the temperatures of investigation could be attributed to the presence of the two methyl side groups in the molecule. This may be because the methyl groups could not easily locate a hole of the appropriate size in the polyethylene matrix at the increased temperatures, and so the diffusion coefficients were lower at 60 and 80°C. In order words, the diffusion of xylene molecules into polyethylene at 60 and 80°C was slower than at 40°C. At all the temperatures investigated, the order of the diffusion coefficients was xylene > toluene > benzene. This order is in the direction of increasing molecular mass volumes and increasing dipole moments of the solvent molecules and also in the direction of decreasing densities and solubility parameters of the solvents, as shown in Table I. In other words, the study reported here showed a dependence of the diffusion coefficient on the nature of the solvent as well as the solvent properties.

Solubility

The sorption coefficient (mol %) was obtained from the plateau regions of the equilibrium sorption and is given in Table II. For the studied solvents, their solubilities in polyethylene films increased with an increase in the sorption temperature from 40 to 80°C. This finding is in agreement with the works of Michaels et al.,[25] who reported that the solubility of solvents in polymers increases with an increase in the temperature. However, the following order of the sorption coefficients could be observed: xylene > toluene > benzene. At 40°C, the solvents benzene and xylene showed similar sorption coefficients (0.28 mol %), with toluene having a lower sorption coefficient (0.26 mol %). Thus, the solvent properties do not seem to have profound effects on the solubility of aromatic solvents in polyethylene, as could be ascertained from the determined solubility values.

Permeability

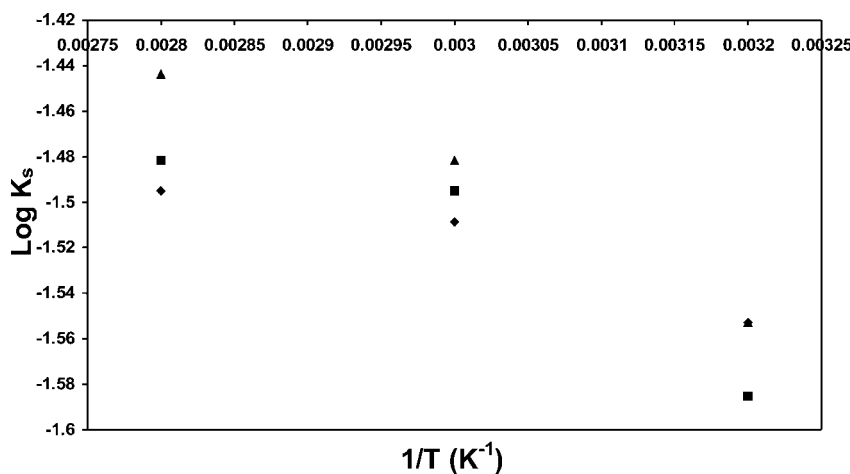The permeability coefficient (P) of the solvents in polyethylene films was obtained as follows:[26]

$$P = D \times S \tag{3}$$

where D is the diffusion coefficient and S is the sorption coefficient. The values of the permeabilities of the solvents (benzene, toluene, and xylene) in polyethylene films at the investigated temperatures are presented in Table II. From Table II, the permeabilities of the solvents benzene and toluene in polyethylene were found to increase from 40 to 80°C. However, the permeability of xylene in polyethylene

TABLE II
Values of the Diffusion Coefficient (D), Sorption Coefficient (S), and Permeability Coefficient (P) of Aromatic Solvents in Polyethylene Films at Different Temperatures

	$D \times 10^5$ (cm²/s)			S (mol %)			$P \times 10^5$ (cm² s⁻¹ mol %)		
Solvent	40°C	60°C	80°C	40°C	60°C	80°C	40°C	60°C	80°C
Benzene	5.388	6.854	8.093	0.28	0.31	0.32	1.508	2.055	2.589
Toluene	7.271	7.365	8.861	0.26	0.32	0.33	1.890	2.357	2.924
Xylene	18.053	8.80	11.430	0.28	0.33	0.36	5.054	2.90	4.114

Figure 4 Plot of log K_S versus $1/T$ for polyethylene in different solvents: ($\blacklozenge$) benzene, ($\blacksquare$) toluene, and ($\blacktriangle$) xylene.

decreased from 40 to 60°C and thereafter increased at 80°C. At any given temperature, the following order of the permeability coefficients could be observed: xylene > toluene > benzene. The permeability of the solvents in polyethylene films showed a dependence on the solvent properties, as reported for the diffusion coefficient.

Activation energy of sorption

To obtain the activation energy of the sorption of the aromatic solvents in polyethylene films, the data for the diffusion coefficient (D) were treated with an Arrhenius-type expression:[31]

$$D = D_0 \exp(-E_D/RT) \qquad (4)$$

where E_D is the activation energy of diffusion into the polyethylene film, D_0 is a pre-exponential factor, and RT has the conventional meaning. Plots of log D against $1/T$ for the studied solvents were drawn, and the calculated activation energies of sorption are presented in Table III. From Table III, it is clear that the activation energies of absorption in polyethylene films were all positive, and the solvents benzene and toluene showed comparable E_D values, with xylene showing a slightly lower E_D value. Ordinarily, xylene is expected to show the highest E_D value because it has the largest molecular size and benzene has the lowest. The converse was, however, obtained, and this may be due to the influence of the molecular structure on the diffusion process. Xylene has two methyl side groups present in its molecule, whereas benzene has none. The data in Table III indicate that the E_D values of the aromatic solvents in polyethylene films are dependent on the solvent properties, densities, and solubility parameters and are inversely related to the molecular mass volumes and dipole moments of the solvents.

Equilibrium absorption constant (K_S)

K_S of the solvents in polyethylene at the investigated temperatures was determined as follows:[32]

K_S = Number of moles of the solvent absorbed

at equilibrium/Mass of the polyethylene sample   (5)

The obtained data were used in calculating the enthalpy of absorption (ΔH_S) and the entropy of absorption (ΔS) in polyethylene films. The values of K_S were substituted into the van't Hoffs equation:[31]

$$\log K_S = \Delta S/2.303R - \Delta H_S/2.303RT \qquad (6)$$

Plots of log K_S against $1/T$ are shown in Figure 4; ΔS and ΔH_S were obtained from the intercepts and slopes of the linear plots and are shown in Table III. ΔH_S is positive, and it increases with an increase in the penetrant size and the dipole moment of the solvents. This may mean that ΔH_S of the aromatic solvents for polyethylene films is dependent on the solvent properties. ΔH_S is a composite parameter involving contributions (1) from Henry's law, which is needed for the formation of a site and the dissolution of the species into that site (the formation of the site involves an endothermic contribution), and (2) from Langmuir's (hole-filling) sorption mechanism,

TABLE III
Values of E_D, ΔH_S, ΔS, and ΔG_S for Aromatic Solvents in Polyethylene Films

Solvent	E_D (kJ/mol)	ΔH_S (kJ/mol)	ΔS (J/mol)	ΔG_S (kJ/mol)
Benzene	26.64	2.77	−20.77	9.27
Toluene	26.22	5.0	−14.25	9.46
Xylene	24.99	5.22	−12.33	9.08

in which case the site already exists in the polymer matrix and sorption by hole filling yields exothermic heat of sorption. In this study, the positive ΔH_S values obtained for the aromatic solvents suggest that sorption in this case is dominated by Henry's mode with an endothermic contribution. The negative ΔS values obtained for the solvents benzene, toluene, and xylene show that the sorbed solvent molecules remain in the liquid state in the polymer matrix.[8] The ΔS values were highest in xylene, which was followed by toluene and then benzene.

Gibbs free energy of sorption (ΔG_S)

The change in ΔG_S of the aromatic solvents in polyethylene films was obtained with the following expression:

$$\Delta G_S = \Delta H_S - T\Delta S \qquad (7)$$

where T is the Kelvin temperature. The values of ΔH_S and ΔS earlier determined for the solvents were substituted into eq. (7), and the calculated values of ΔG_S are shown in Table III for the solvents benzene, toluene, and xylene. The calculated ΔG_S values were all positive, and this was an indication of the nonspontaneity of the solubility of polyethylene in the aromatic solvents at 313k. The solvents benzene, toluene, and xylene showed similar ΔG_S values, and this indicated that the change in ΔG_S of the aromatic solvents in polyethylene films may be independent of the solvent properties.

CONCLUSIONS

The diffusion coefficients and permeabilities obtained for aromatic solvents (benzene, toluene, and xylene) in polyethylene films increased with an increase in the sorption temperature. The diffusion coefficient was highest for xylene and least for benzene. The solubilities of the solvents in polyethylene films also increased with an increase in the temperature, and at 40°C, there was no observed order in the solubility values among the solvents studied. The calculated activation energies of sorption of the aromatic solvents in polyethylene films showed the following order: benzene > toluene > xylene. The ΔH_S values of the solvents in polyethylene films were positive, whereas the ΔS values were all negative, and the following order for both ΔH_S and ΔS was observed, xylene > toluene > benzene. The calculated free energies of sorption were all positive, and this was an indication of the nonspontaneity of the solubility of polyethylene in the aromatic solvents at 313 K.

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